Molecular-dynamics study of nitrogen impurities in tetrahedral amorphous carbon

Th. Köhler, G. Jungnickel, and Th. Frauenheim

Universität/Gesamthochschule Paderborn, D-33095 Paderborn, Germany

(Received 21 May 1999)

We discuss the properties of nitrogen impurities inside tetrahedral amorphous carbon, *ta*-C. In contrast to previous studies on this subject, we have incorporated the N atoms in the disordered structure during evolution of the amorphous system, which is studied by simulated annealing of a high-temperature carbon-nitrogen phase at various N concentrations between 3 and 11 at. %. We find two- and threefold coordinated nondoping N sites that become stabilized by saturation of lone pair orbitals. These configurations appear to be isoenergetic with other local geometries, which potentially could act as dopants. The latter are either sp^2 -bonded nitrogen atoms with two σ -single and one π -double bond to next-nearest neighbors or sp^3 -hybridized atoms, which develop four σ -single bonds. Doping through these configurations is too difficult to control and should have a low efficiency, since the donated extra electrons can easily migrate to remote π -bonded clusters in the carbon host matrix. Increasing dopant concentration promotes the formation and growth of such clusters which counteracts the desired doping behavior. [S0163-1829(99)02339-5]

I. INTRODUCTION

The outstanding chemical, mechanical, and electronic properties of tetrahedrally bonded carbon material suggest possible applications in electronic devices that could operate under harsh environmental conditions. Considerable experimental efforts in fabricating such carbon thin films aimed to achieve high-electronic quality comparable to the natural allotrope diamond, i.e., material with large band gaps, steep band edges, and lowest defect concentrations. Such a system would be promising to remove some of the problems currently associated with the technological application of diamond. Despite the world-wide success in growing chemical vapor deposition diamond films, the success when trying to dope diamond *n*-type is rather limited. Substitutional nitrogen produces a donor level in natural diamond 1.7 eV below the conduction band,1 too deep in the gap for practical purposes. Phosphorus is less soluble and frequently deactivated by vacancies² so that its doping efficiency is restricted, too.

A dense amorphous structure known as the highly tetrahedral amorphous carbon phase (*ta*-C) (Ref. 3) has been considered as an alternative material to solve the doping problem in carbon while showing similar physical properties as diamond itself. Electronically, the disordered material is characterized by very large (2 to 3 eV) and direct band gaps^{4–6} and thus has prospects for both *n*- and *p*-type doping.

The outstanding physical properties of *ta*-C arise from the predominance of up to 80% sp^3 -hybridized atoms, which locally maintain a diamondlike fourfold coordinated configuration. The reduction of the band gap compared to diamond is a consequence of the remaining lower coordinated atoms, which almost exclusively take part within isolated small π -bonded clusters or sp^2 -bonded dimers inside the material.^{7,8} Such clusters introduce additional (π - π^*) states with energies in the fundamental gap region of the σ - σ^* states made up by the diamondlike matrix. Therefore, the band gap width is about 40 to 60% that of diamond. A variety of experiments have been performed to dope *ta*-C with N.⁹⁻¹⁴ Whether efficient doping has really been

achieved is, however, controversial. Veerasamy *et al.*¹⁰ claimed success using both phosphorus and nitrogen atoms as dopants, and they observed a pronounced increase of the conductivity together with a transition from intrinsic *p*-type to *n*-type behavior for their arc-deposited material. In contrast, Ronning *et al.*¹² attribute similar observations for their *ta*-C films prepared by ion-beam deposition to hopping transport via localized states at the Fermi energy rather than to transport caused by excitation of doping levels.

At lowest doping concentrations (<1 at %) the dominant tetrahedral sp^3 -bonded network is believed to remain intact while heavily doped material shows a pronounced increase of the sp^2 -carbon content.^{13,15} As a result the π -clusters inside the network tend to become larger. The π - π *-gap decreases and the doping quality of the *ta*-C films becomes reduced.

The extreme limit of very large nitrogen content is the amorphous carbon nitride structure, which is found when attempting to deposit (see Ref. 16 and references therein) the proposed hypothetical C_3N_4 crystalline phase.¹⁷ The amorphous carbon nitride system typically shows a mass density, which compared to an analogous *ta*-C film with low-nitrogen concentration is significantly reduced by about 30%. A theoretical study of this system¹⁸ showed in agreement with experiments that the number of carbon atoms in a local configuration that deviates substantially from diamondlike fourfold coordination is largely dependent on the nitrogen content. The stiffness of the network becomes drastically reduced with increasing *N* content due to a breakdown of cross links between carbon atoms and the occurrence of embedded *N*-terminated chain segments.

The reduction of the sp^3 fraction already at small N concentrations in *ta*-C and the experimentally observed low doping efficiency requires a more fundamental atomistic understanding. Although changes in conductivity of the material seem to be correlated with the nitrogen content and, hence, could possibly be controlled, there is still an uncertainty concerning the doping and the conduction mechanisms.

Recent theoretical investigations using density-functional-

10 864

based molecular dynamics (DF-MD) have shed some light into the possible N-doping configurations within a ta-C matrix. The properties of N impurities substituted into existing models of amorphous carbon have been reported by Stumm et al.7 using the multicenter "ab initio" tight-binding technique and Sitch et al.8 using the two-center densityfunctional-based tight-binding (DFTB) method. Both studies agree, that in ta-C a potential acceptor or donor level is in strong competition with bonding and antibonding states associated with the π -orbital overlap between threefoldcoordinated carbon atoms. Such atoms form even membered π -bonded clusters of small size, preferably dimers that electronically are isolated within the otherwise fourfold coordinated matrix. The size distribution of such clusters together with strain effects cause the associated electronic π states to form broad bands with long tails within the σ - σ^* gap of the host network. In these early doping models, the tails of the π bands range to energies where potential acceptor and donor levels should appear. It has been observed that the injected hole or electron as a consequence migrates to either an occupied high-energy π or an unoccupied low-energy π^* level of the carbon matrix, respectively. This induces substantial relaxation at the associated π cluster and the Fermi level is frequently pinned at a partially filled, localized deep carbon state. In such a situation conductivity should be possible only through variable range hopping.^{8,12}

Full self-consistent field calculations have been reported subsequently based upon density-functional theory,¹⁹ which basically support the mentioned tight-binding findings. The picture obtained in all of the studies, however, rests upon the assumption that the connectivity of the amorphous host network is not remarkably altered by the substitutional impurity so that there is only little local relaxation in its neighborhood. A systematic study of higher doping concentrations is difficult within a decoration technique due to the unknown spatial distribution of the impurities and the overall structural changes that are induced during growth.

In this paper, we report on the generation of nitrogenated amorphous carbon models by the same simulated annealing techniques previously used to successfully model amorphous carbon systems at various mass densities⁴ by molecular dynamics. This methodology allows the nitrogen atoms to find the preferred bonding configurations and distributions in the network during the evolution of the structure starting from a high-temperature phase. The properties of the models will then depend on the mass density, the atom concentrations, and the annealing rate.

The paper is organized as follows. We first briefly review our results obtained by model decoration with nitrogen in Sec. II. In Sec. III, we explicitly describe the modeling techniques used for this study and discuss the results in comparison to the previous investigations in Sec. IV. We find that various nitrogen bonding configurations coexist in the material. We show that one of them, which previously has been discarded based on the energetics in decoration studies in reality appears to be the most likely local geometry. We identify doping situations on a local scale but need to conclude in Sec. V that these are rendered unimportant for the total system on the same grounds of overlap between the dopant levels and the band tails of carbon π^* orbitals as found during the decoration studies.

II. SUMMARY OF SUBSTITUTIONAL INVESTIGATIONS

For the decoration studies⁸ we have used a model structure for *ta*-C which had been carefully annealed starting from a high-temperature liquidlike state. The model had similar binding statistics as those previously studied in great detail⁴ but was particularly interesting since it did not show any deep carbon defect level after the annealing, which is the required defect density for the size of the model (128 atoms) structure.

The *ta*-C structure without the carbon defect states is characterized by very steep band edges, narrow π and π^* bands, and a large band gap of about 2.4 eV. We substituted both boron and nitrogen for various sites of the amorphous matrix. Finally, we annealed the structures for 2 ps at a constant temperature of 1000 K and relaxed the very last molecular-dynamics configuration using a conjugate gradient technique to obtain a forcefree metastable model.

We observed that the most stable site for the N atom is a stretched sp^3 site. The longest bond broke during post relaxation, which left the N atom threefold coordinated with distorted σ bonds of lengths 1.57, 1.53, and 1.48 Å and a lone pair of electrons, as indicated by a Mulliken charge analysis. Connected with this we found a migration of charge from the newly created threefold coordinated nearest-neighbor C atom to a π cluster nearby in the amorphous matrix occupying the lowest available π^* state. This caused considerable relaxation of atoms in this π cluster moving the singly occupied state towards midgap where it pinned the Fermi energy 0.6 eV above the π valence band top.

In addition, a relatively undistorted sp^3 site was determined to be metastable with an energy of incorporation for the N atom being 0.54 eV higher than that of the minimum energy cluster mentioned above. There, the N atom remained fourfold coordinated and fully sp^3 bonded with back bond lengths 1.46, 1.54, 1.47, and 1.42 Å. We recognized that in this case charge migrates from the N atom to remote π clusters to stabilize this configuration. The resultant localized partially filled defect level appeared 0.7 eV above the π valence-band top.

Substitution for a π -bonded carbon site was found to be unstable, the N atom spontaneously broke the π bond and transformed into the electronically saturated threefold σ bonded plus lone pair N site. As a consequence, the unsaturated electron left at the former neighbor now was able to migrate and caused structural relaxations in π clusters nearby.

As mentioned above, the doping studies described so far are based upon substitutional modifications of a pre-existing model structure of tetrahedral amorphous carbon. This might not have given a true overall picture of the doping situation. In order to remove unphysical bias from the former results in particular with respect to local dopant bonding and to make a better link to experiments where dopants are incorporated during growth of the amorphous films it is desirable to carefully study the full evolution of nitrogenated *ta*-C models in dependence on the doping concentration. This should reduce uncertainties concerning the occurance and relative stability of particular local configurations.

As mentioned above, typical relaxation processes in postsubstitution studies envolve charge migration to remote carbon π clusters. It is an open question if such states really are accessable when the charge is present during evolution of the carbon host network. Usually, carbon during dynamic formation tends to completely avoid the creation of partially filled defect states and it may be therefore possible that the whole matrix differs significantly from the decoration investigations in order to screen the injected charge.

Based upon the recent MD studies of structure formation in high-density carbon nitrides $C_x N_y$,¹⁸ we also expect that threefold coordinated nitrogen atoms that form a strong π bond to one of the *C*-neighbors will become stabilized rather than destabilized as the substitution studies suggest. Finally, it is unclear whether twofold coordinated nitrogen atoms do exist for low N concentrations, too, and if they would significantly change the global picture concerning *n*-type doping obtained so far.

III. MODELLING TECHNIQUES

We have generated seven *ta*-C:N models at a fixed mass density of 3.0 g/cm³ with *N*-fractions between 3 and 11 at. %. Using Γ -point Brillouin-zone sampling for total energy calculations in sufficiently large three-dimensional periodic supercells the interatomic forces are obtained by means of the DFTB scheme.^{20,21} This method has been shown to be transferable to systems of various type and scale and successful in modeling heteroatom interactions with C, H, B, and N, too.^{8,18,22} In any case, we started from a random atom distribution representing a high-temperature phase of the given stoichiometry and density.

At first, the models were equilibrated by NVT molecular dynamics for 0.5 ps at 8000 K. Low-energy amorphous structures were then obtained by simulated annealing to room temperature with a cooling rate of 3850 K/ps. The models were then equilibrated again at 300 K for another 1 ps and no significant further changes of the structure were observed. The last molecular-dynamics snapshot structures were finally post relaxed by a conjugate gradient algorithm to establish representative local minima of the energy land-scape for each given nitrogen content.

IV. STRUCTURE AND ELECTRONIC PROPERTIES OF N-DOPED TA-C

In Fig. 1, we compare total reduced radial distribution functions (RDF) for neutron scattering of a pure *ta*-C model, which has been shown to coincide with experimental data⁴ and of nitrogenated amorphous carbon models. Here, the N concentrations range from the highest content considered for the electronic part of this doping study to a concentration, which would be equivalent to the hypothetical crystalline C_3N_4 phase at the mass density 3.0 g/cm.³

The functions shown are the Fourier transforms of the interference functions $F(Q) = Q \times [S(Q) - 1]$, which in scattering experiments are derived from the respective structure factors S(Q) of systems under consideration. They have been convoluted by Gaussians of finite width to reduce noise and to simulate experimental broadening.

The figure contains the partial carbon-carbon correlation functions (dotted lines), which contribute to the total distribution function. It shows that structural differences between



FIG. 1. The Radial distribution function of amorphous models at 3.0 g/cm^3 for various N concentrations reveals a decrease of the coordination number (area of first peak) and the occurrence of a distinct feature at a correlation length of about 3 Å with increasing nitrogen content.

the nitrogenfree ta-C model and a system, which already contains 11 at. % N are quite small. In this case, the partial C-C correlation contributes to the full distribution function by about 97%. Hence, static properties of material with lowdopant concentration are expected to be very similar to those of pure ta-C. Further increasing the nitrogen content causes the position of the first peak of the RDF to shift to shorter correlation lengths. This indicates that the average bond lengths in the amorphous structure becomes reduced. A similar significant shift of the peak position to shorter distances is observed for the second major peaks, which mostly depend on the distribution of second nearest neighbors. These are frequently associated with a decrease of the average bond length and/or bond angle. Such an interpretation neglects, however, that correlations between third and fourth neighbors can significantly influence the RDF of this region.

It is worth noting that the C-C partial correlation becomes dramatically changed with large nitrogen content indicating the breakdown of the carbon host matrix. We particularly want to stress a fingerprint subpeak at about 3 Å, which increases when the nitrogen content is getting larger. By analyzing the RDF's with respect to the hybridization type of atoms we find the correlations of this particular distance superposed by a variety of contributions.

For a more detailed analysis, we follow Stephan *et al.*⁶ and determine the hybrid fractions of incorporated C and N atoms individually. Within this analysis sp^m (m=1,2,3) denotes atoms that appear to be coordinated in an idealized manner so that the local electronic density of states is very similar to analogous atoms in perfectly hybridized reference

TABLE I. Hybrid fractions of carbon atoms.

N content [at. %]	<i>sp</i> ¹ [%]	<i>sp</i> ² [%]	<i>sp</i> ³ [%]	$sp^{(1+x)}$ [%]	$sp^{(2+x)}$ [%]
0.0	0.0	20.3	69.5	0.8	9.4
3.0	0.0	29.7	58.6	1.6	9.4
5.9	0.0	25.8	61.7	0.8	11.7
7.2	0.0	32.8	53.9	3.1	9.4
8.6	0.0	36.7	51.6	3.1	8.6
9.9	0.0	33.6	49.2	4.7	12.5
11.1	0.0	46.1	40.6	3.1	10.2
33.3	2.1	52.1	33.3	2.1	8.3
57.1	5.0	53.3	23.3	0.0	5.0

systems such as crystals. In contrast $sp^{(1+x)}$ or $sp^{(2+x)}$ indicate substantial deviation from the ideal hybrid geometry. The full hybrid statistics for carbon and nitrogen atoms are summerized in Tables I and II, respectively. Note that atoms that terminate paths in the network are not listed in the tables.

The sp^3 - sp^3 , sp^2 - sp^2 , sp^3 - sp^2 correlations exclusively determine the RDF for nitrogen-free models without defect states. Increasing the nitrogen content renders these contributions less important while correlations with $sp^{(1+x)}$ and $sp^{(2+x)}$ type of atoms become dominating. This is particularly the case for the fingerprint region and clearly expresses the capability of nitrogen atoms to favor low atom coordination and chainlike features in the structures. The partial C-C correlation function where the area under the first peak is a measure of the carbon-carbon coordination number is dramatically reduced for very large nitrogen content. According to Table I sp^1 -type carbon atoms only occur for very large N content, which agrees with experimental observations by Zhang *et al.*²³

Concerning structures with moderate and low *N* content we find no such carbon species. This supports the experimental findings by Hu, Yang, and Lieber¹⁶ using infrared spectroscopy. However, for all systems investigated around 3% of the carbon atoms occur in a distorted $sp^{(1+x)}$ and about 10% in a $sp^{(2+x)}$ configuration. While the amount of well relaxed sp^2 -type carbon atoms increases with nitrogen content from about 20 to 46 % the number of sp^3 -like carbons decreases by nearly the same rate from about 70 to

TABLE II. Hybrid fractions of nitrogen atoms.

N content	sp^1	sp^2	sp^3	$sp^{(1+x)}$	$sp^{(2+x)}$
[at. %]	[%]	[%]	[%]	[%]	[%]
0.0	0.0	0.0	0.0	0.0	0.0
3.0	0.0	50.0	0.0	25.0	25.0
5.9	0.0	50.0	25.0	25.0	0.0
7.2	0.0	40.0	10.0	20.0	30.0
8.6	0.0	25.0	16.7	33.3	25.0
9.9	0.0	64.3	14.3	7.1	14.3
11.1	0.0	62.5	12.5	12.5	12.5
33.3	2.1	33.3	0.0	39.6	18.8
57.1	2.5	12.5	0.0	45.0	3.8

TABLE III. Average numbers of *j* atoms in the neighborhood of *i*-type atoms, k_{ij} .

N content [at. %]	k _{CC}	k _{CN}	k _{NC}	k _{NN}
0.0	3.69			
3.0	3.48	0.09	2.75	0.00
5.9	3.42	0.19	3.00	0.00
7.2	3.27	0.23	2.90	0.00
8.6	3.22	0.27	2.83	0.00
9.9	3.11	0.34	3.07	0.00
11.1	3.00	0.38	3.00	0.00
33.3	2.02	1.23	2.46	0.00
57.1	0.63	2.28	1.71	0.03

41 %, see Table I. Hu, Yang, and Lieber¹⁶ during electron energy loss spectroscopy measurements have recently identified a very similar nitrogen induced transformation of the carbon hybrids. In their systematic study of nitrogen incorporation into films obtained by pulsed laser deposition they found that above 20 at. % nitrogen almost no carbon atom is left in an sp^3 -bonded state. There, however, the density of the films decreased significantly during nitrogen incorporation to facilitate such a strong effect. In our study, the density is kept constant for all models that hinders a further decrease in carbon sp^3 content.

The trends for the nitrogen atoms are less clear. However, when the nitrogen concentration is very low or very large it is unlikely to find N atoms with four neighbors in sp^3 -type configurations. This appears to be different for moderate N concentrations. A large number of $sp^{(2+x)}$ -type configurations indicates the existence of threefold coordinated nitrogen with a considerable deviation from an ideal hybrid geometry. Such species dissapear for more than 50 at. % nitrogen where N atoms seem to prefer a sp^2 or $sp^{(1+x)}$ configuration or terminate chains in the network.

Table III details the coordination numbers for the various bond partners in the models. The table supports the observed trends already found in analyzing the RDF's that the carboncarbon coordination becomes reduced when the nitrogen content increases. Note, however, that the total carbon coordination remains almost constant for lower nitrogen concentrations. What is surprising here, is, that nitrogen atoms clearly avoid to bond with each other.

Such an observation would be hard to infer from a decoration of existing models and shows the importance of the present investigation as compared with previous studies. Also, for low-nitrogen concentration *N*-atoms are surrounded by three carbon atoms on average. Considering the large numbers of sp^{2} - and $sp^{(2+x)}$ -type of N atoms this indicates that nitrogen atoms prefer perfect isolation within the host material.

In the following we concentrate on the electronic consequences of the structural properties summarized in the Tables I, II, and III. In connection with applications in electronics the various local configurations at the N sites need to be categorized according to their potential for doping. We can subdivide the local structures into configurations that electronically represent fully saturated and, hence, nondoping states and those with possible doping states. The first group contains N atoms that are either marked $sp^{(2+x)}$ bonded such that nitrogen is threefold coordinated or $sp^{(1+x)}$ bonded so that N is twofold coordinated both with substantial deviations from respective optimal hybrid geometries. Nitrogen in an $sp^{(2+x)}$ configuration typically forms three single σ bonds to the carbon neighbors with bond lengths that are almost identical (around 1.45) Å. This would be true for sp^2 hybrids, too. Appreciable distortions of the local structure are due to a nonplanar bonding arrangement with a gradual transition to sp^3 character. In an ordinary tetrahedral semiconductor this would cause partially filled defect states to appear at midgap.

In the *ta*-C:N system it is possible to stabilize these local configuration by saturating the associated nitrogen level under creation of a lone-pair electron state that lies at the valence-band edge. In this configuration the extra electron injected by the nitrogen atom is completely deactivated by the special arrangement of the N site in the carbon host.

In contrast, N- $sp^{(1+x)}$ atoms form two bonds to their two carbon neighbors, which can be very different with respect to the bond lengths. In the majority of cases one of the two bonds is a single σ - and the other a typical π -double bond with respective lengths of about 1.45 and 1.30 Å. This local structure saturates three electrons associated with the nitrogen center and is then stabilized by the creation of a lonepair state in order to screen the extra charge. In very rare occasions the matrix can prevent the creation of the wellrelaxed π -double bond between the impurity and the neighbors. Then the local configuration tends to have two σ bonds both with partial π contributions. Such bonds have almost equal length of about 1.40 Å and saturate four electrons. The remaining nitrogen electron captures another electron from available higher levels and again establishes a lone-pair state.

In either case the lone-pair electrons electrostatically repel the bonding electrons, which causes the substantial distortion of the hybrid geometry. The lone-pair orbitals are localized at the impurities and the associated charge distribution reaches into empty regions in the surrounding network. Figure 2 shows the local electronic density of states (LDOS) at N atoms representative for the two major bonding situations discussed above for the model with 6 at. % nitrogen inside.

The figures show that for $sp^{(1+x)}$ -bonded nitrogen atoms the Fermi energy lies midgap between valence π and π^* bands, which are primarily generated by the surrounding carbon material. This is comparable with the common nondoped *ta*-C groundstate and, therefore, less important for electronic applications. For completeness we note that in reality undoped *ta*-C structures are found to be intrinsically *p*-type,¹⁰ which arises from localized carbon defect states pinning the Fermi level a little below midgap.

Nitrogen sites with $sp^{(2+x)}$ character appear to enhance such a trend. The Fermi energy of the full system is very close to the LDOS valence-band edge for these species. The ground state has two electrons in a lone-pair level and three almost identical single σ bonds. An alternative state where one of the lone-pair electrons is captured to turn an existing single bond at the N site into a full and shortened π -double bond leaving an electron behind, which needs to migrate to a localized deep state at the Fermi level seems to be less likely to exist. Note the small peak in Fig. 2 for the $sp^{(2+x)}$ case that indicates an already existing unoccupied state with



FIG. 2. Local geometry and LDOS split into s (dotted) and p (dashed) contributions for representative nitrogen impurities (black) in nondoping lone-pair configurations. The bonding environment of carbon (dark) and nitrogen (light) neighbors leaves no defects in the LDOS gap region.

strong *p* character due to overlapping atomic orbitals close to the N atom. This molecular orbital might turn into a π bond in the alternate occupation scheme as a result of an excitation on the cost of loosing one of the lone-pair electrons for a partially filled deep defect level. In our calculations, however, the ground states of the structures with low- and moderate-N content seem to be characterized by gain of some energy as a result of avoiding such partially filled π bonds in favor of saturated lone-pair electron orbitals.

In conclusion, we can clearly identify local bonding configurations in which nitrogen forms lone-pair electrons such that associated molecular orbitals are completely saturated and where the nitrogen extra electrons are, hence, totally deactivated. Therefore, these cannot contribute to *n*-type doping in *ta*-C. In contrast to the previous decoration studies we have little evidence for the proposed deep state due to a carbon dangling bond adjacent to the nitrogen impurity. This result was biased by the simulation scheme and caused by incomplete relaxation of the impurity and its neighbors in the pre-existing carbon matrix. The energetically unfavourable situation occurred there because of bond breaking induced by the post substitution of an N atom in a local surrounding, which in reality would not exist.

Next, we consider the remaining nitrogen atoms with local structures, which should have potential for doping and are not easily deactivated by appropriate relaxation of the impurity itself. Such configurations are expected at sites with almost ideal sp^2 - and sp^3 -hybrid geometry.

The sp^3 type N's have four almost equivalent σ bonds to their C neighbors with bond lengths in the region of 1.43 to 1.53 Å. The local structure is typical for tetrahedral bonding. The sp^2 -hybridized nitrogen atoms in contrast develop planar geometries with two σ -single (\approx 1.45-Å long) and one shorter π -double bond (\approx 1.30-Å long) to their neighbors.

Figure 3 shows the respective local electronic DOS at corresponding representative atoms, again for the model with 6 at. % nitrogen inside. The LDOS of the sp^2 -hybridized nitrogen atom shows a pronounced π - π^* state that arises



FIG. 3. Local geometry and LDOS for representative nitrogen atoms in configurations with potential for doping, notations as in Fig. 2. Note, the obvious shift of the Fermi energy towards the π^* band in the sp^2 -hybridized case.

from the π -double bond nearby. The Fermi energy is shifted a little towards the unoccupied π^* bands. This is the desired effect for a true donor state near this band edge. The extra electron injected may naively be expected to be still localized near the N site. A participation analysis of the highest occupied (HOMO) orbitals reveals, however, that the HO-MO's in all of our models are largely due to *p*-type atomic orbitals localized at single carbon atoms. These carbon species are in $sp^{(2+x)}$ configurations and contribute with about 50% to the highest molecular orbitals. This is the same unfortunate situation found in the previous studies and due to the migration of charge away from the nitrogen impurities into localized carbon states, which without dopants would not be occupied.

True doping behavior could still be obtained if the lowest unoccupied molecular orbitals (LUMO's) were delocalized conduction bands. However, control over doping would be limited due to disorder induced fluctuations of the energy of the carbon levels trapping the injected charges. We find by the same partizipation analysis that the LUMO's are largely due to a few carbon atoms almost equally contributing to these states. Associated atom configurations typically include isolated strained carbon-carbon π bonds and nonbonded defects, again localized at single carbon atoms. The LUMO's in our models do, therefore, not have any appreciable delocalized character.

We also analyzed the next states below and above the Fermi energy in detail for the model with 6 at. % nitrogen. We find in this particular case that the sixth molecular orbital above the Fermi level is the first showing significant contributions from numerous atoms throughout the supercell including a few nitrogen atoms. It is difficult to obtain the true location of this level with respect to the Fermi energy given uncertainties of a minimal basis set approach when describing unoccupied orbitals. We estimate this difference to be about 1.6 eV, which is far beyond any useful shallow doping situation. Doping in the classical sense is, therefore, unlikely to occur. The energy differences between the localized lev-



FIG. 4. Total electronic densities of states (DOS) of a-CN models vs N content. Curves are referenced with respect to the Fermi energies (dotted line). Note a slight change of the symmetry of the bands close to the Fermi level with increasing content.

els, which appear below this conduction-band state are all less than 0.7 eV typically around 0.3 eV. We, therefore, conclude, that hopping transport may be promoted already at room temperature.

Post substitution of nitrogen into a π bonded C- sp^2 site of an existing ta-C model resulted in an fairly unfavorable N incorporation.⁸ In full contrast, we find in this study that the π -bonded sp^2 -N sites are by far the most likely local structure for nitrogen atoms in an amorphous carbon host matrix. About 50% of the nitrogen atoms incorporated in situ by molecular dynamics prefer this bonding configuration. Moreover, this local structure has good potential for true doping. This has been shown recently in a theoretical study of nitrogen doping in hypothetical purely sp^2 -bonded crystalline forms of carbon.²⁴ In these structures all carbon π states result from equivalent π bonds, which loosely interact such that the π^* bands are flat and above the impurity level. In contrast to the situation in these allotropes, the electron levels in the amorphous models associated with impurities become emptied since carbon π^* states in the disordered host material can lie below the desired doping levels. The broadening of the π^* bands due to the disorder in the material deactivates the nitrogen impurities.

For the remaining sp^3 -hybridized nitrogen sites the doping efficiency has already been analyzed in the decoration studies. It has been detected to be extremely limited since the injected electrons migrate to remote π clusters, too, causing structural rearrangements and leaving the electrons in lower-

Finally, we present the total electronic densities of states for the models with low- and moderate-doping concentration in Fig. 4. Note, that the height of peaks associated with the bonding π and the antibonding π^* bands near the Fermi level is not significantly increased when the nitrogen content rises. Therefore, the observed enhancement of π bonding in the network is essentially covered by disorder-induced broadening of the associated bands. This results in the shrinkage of the HOMO-LUMO-gaps when the nitrogen content increases and explains the frequent deactivation of possible dopant sites by charge migration into the band tails. The change of the symmetry of bands near the Fermi energy suggests a slight shift of this level towards the unoccupied π^* states when the nitrogen content goes up. Considering the uncertainties of the minimal basis set approach in which unoccupied bands usually are moved to higher energies this effect in reality may be more pronounced than can be inferred from Fig. 4. Therefore, our models do not contradict experiments¹¹ where such a shift has been detected.

V. CONCLUSIONS

Small and moderate concentrations of nitrogen impurities have been studied in amorphous carbon models with a density typical for the tetrahedrally bonded form of this disordered material (*ta*-C). The simulations have been performed entirely by *in situ* incorporation of the dopants into structures evolving from a high-temperature phase by simulatedannealing within molecular dynamics employing the densityfunctional-based tight-binding method to calculate the interatomic forces.

We find that nitrogen remarkably enhances the π -bonded subnetwork of the models and simultaneously causes the fraction of carbon atoms in a tetrahedral sp^3 -like local geometry to decrease. This is not only the case for very large nitrogen concentrations (> 11 at. %) as observed previously but also true for lower impurity contents.

This process counteracts the desirable doping properties of tetrahedrally bonded high-density amorphous carbon and limits its potential for electronic applications.

Nitrogen atoms in the annealed structures favor a complete surrounding by carbon and can be found almost isoenergetically in both nondoping and potential doping sites. We found two types of nondoping nitrogen impurities, which both are characterized by the formation of electronically saturated lone-pairs orbitals. In this case, the impurity lends itself to become deactivated.

The two local nitrogen configurations that potentially could be useful in connection with doping are the fourfold coordinated sp^3 -hybrid and a threefold-coordinated sp^2 -hybrid geometry with one additional π bond to a carbon neighbor, which was previously discarded based on the energetics in post substitution of existing *ta*-C models. In contrast, based on the present study such a threefold nitrogen impurity appears to exist with overwhelming majority.

Associated local configurations satisfy four of the nitrogen electrons by creation of four σ -single $(sp^3 \text{ case})$ or two σ -single and one π -double bond $(sp^2 \text{ case})$ to the carbon neighbors. The remaining nitrogen electron easily migrates away from the impurity to either a localized carbon defect where it is trapped or to a carbon π^* state deeper in the gap than the nitrogen donor level. Long tails of the π^* bands, hence, overlap with the potential donor states such that they become deactivated.

As the consequence, depending on the actual position of the classical doping level a considerable amount of the electrons injected by nitrogen are donated into remote carbon π clusters. The rest stabilizes the nondoping configurations by filling lone-pair orbitals. As a matter of fact the extra charges are always donated into energetically lower-lying states in all of our models.

The Fermi energy appears to undergo a slight shift towards the conduction bands with increasing nitrogen content but this must be attributed to the structural changes in the network rather than to true *n*-type doping.

A careful analysis of the molecular orbitals near the Fermi energy shows that these states are primarily superposed by strongly localized orbitals of carbon atoms supporting the overall picture. The energy differences between these states support the picture that transport appears to be only possible by variable range hopping, which may be activated already at room temperature.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the Deutsche Forschungsgemeinschaft and the trinational D-A-CH cooperation.

- ¹Semiconductors: Group IV Elements and III-V Compounds, edited by O. Madelung (Springer, Berlin, 1991).
- ²R. Jones, J. E. Lowther, and J. Goss, Appl. Phys. Lett. **69**, 2489 (1996).
- ³D. R. Mckenzie, D. A. Muller, and B. A. Pailthorpe, Phys. Rev. Lett. **67**, 773 (1991).
- ⁴G. Jungnickel, M. Kühn, S. Deutschmann, F. Richter, U. Stephan, and Th. Frauenheim, Diamond Relat. Mater. **3**, 1056 (1994); Th. Frauenheim, G. Jungnickel, Th. Köhler, and U. Stephan, J. Non-Cryst. Solids **182**, 186 (1995), and references therein.
- ⁵D. A. Drabold, P. D. Fedders, and P. Stumm, Phys. Rev. B **49**, 16 415 (1994).

- ⁶U. Stephan, Th. Frauenheim, P. Blaudeck, and G. Jungnickel, Phys. Rev. B **50**, 1489 (1994).
- ⁷P. Stumm and D. A. Drabold, Solid State Commun. **93**, 617 (1995); P. Stumm, D. A. Drabold, and P. A. Fedders, J. Appl. Phys. **81**, 1289 (1997).
- ⁸P. K. Sitch, Th. Köhler, G. Jungnickel, D. Porezag, and Th. Frauenheim, Solid State Commun. **100**, 549 (1996); P. K. Sitch, G. Jungnickel, Th. Köhler, Th. Frauenheim, and D. Porezag, J. Non-Cryst. Solids **227–230**, 607 (1998).
- ⁹G. A. J. Amaratunga, J. Robertson, V. S. Veerasamy, W. I. Milne, and D. R. Mckenzie, Diamond Relat. Mater. 4, 637 (1995).
- ¹⁰V. S. Veerasamy, G. A. J. Amaratunga, C. A. Davis, A. E. Timbs,

W. I. Milne, and D. R. Mckenzie, J. Phys.: Condens. Matter 5, L169 (1993).

- ¹¹V. S. Veerasamy, J. Yuan, G. A. J. Amaratunga, W. I. Milne, K. W. R. Gilkes, M. Weiler, and L. M. Brown, Phys. Rev. B 48, 17 954 (1993).
- ¹²C. Ronning, U. Griesmeier, M. Gross, H. C. Hofsäss, R. G. Downing, and G. P. Lamaze, Diamond Relat. Mater. 4, 666 (1995).
- ¹³C. A. Davis, D. R. Mckenzie, Y. Yin, E. Kravtchinskaia, G. A. J. Amaratunga, and V. S. Veerasamy, Philos. Mag. B 69, 1133 (1994).
- ¹⁴C. A. Davis, Y. Yin, D. R. Mckenzie, L. E. Hall, E. Kravtchinskaia, V. Keast, G. A. J. Amaratunga, and V. S. Veerasamy, J. Non-Cryst. Solids **170**, 46 (1994).
- ¹⁵S. R. P. Silva, B. Rafferty, G. A. J. Amaratunga, J. Schwan, D. F. Franceschini, and L. M. Brown, Diamond Relat. Mater. 5, 401 (1996).

- ¹⁶J. Hu, P. Yang, and C. M. Lieber, Phys. Rev. B 57, R3185 (1998).
- ¹⁷A. Y. Liu and M. L. Cohen, Science **245**, 841 (1989).
- ¹⁸F. Weich, J. Widany, and Th. Frauenheim, Phys. Rev. Lett. **78**, 3326 (1997).
- ¹⁹S. Pöykkö, M. Kaukonen, M. J. Puska, and R. M. Nieminen, Comput. Mater. Sci. **10**, 351 (1998).
- ²⁰D. Porezag, Th. Frauenheim, Th. Köhler, G. Seifert, and R. Kaschner, Phys. Rev. B **51**, 12 947 (1995).
- ²¹G. Seifert, D. Porezag, and Th. Frauenheim, Int. J. Quantum Chem. **98**, 185 (1996).
- ²²J. Widany, F. Weich, Th. Köhler, D. Porezag, and Th. Frauenheim, Diamond Relat. Mater. 5, 1031 (1996).
- ²³Z. J. Zhang, S. Fan, J. Huang, and C. M. Lieber, Appl. Phys. Lett. 68, 2639 (1996).
- ²⁴G. Jungnickel, P. K. Sitch, Th. Frauenheim, B. R. Eggen, M. I. Heggie, C. D. Latham, and C. S. G. Cousins, Phys. Rev. B 57, R661 (1998).